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Rapid depletion of dissolved organic sulphur (DOS) in freshwaters

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Abstract Sulphur (S) is a key macronutrient for all organisms, with similar cellular requirements to that of phosphorus (P). Studies of S cycling have often focused on the inorganic fraction, however, there is strong evidence to suggest that freshwater microorganisms may also access dissolved organic S (DOS) compounds (e.g. S-containing amino acids). The aim of this study was to compare the relative concentration and depletion rates of organic ^{35}S -labelled amino acids (cysteine, methionine) with inorganic S ($\text{Na}_2^{35}\text{SO}_4$) in

oligotrophic versus mesotrophic river waters draining from low nutrient input and moderate nutrient input land uses respectively. Our results showed that inorganic SO_4^{2-} was present in the water column at much higher concentrations than free amino acids. In contrast to SO_4^{2-} , however, cysteine and methionine were both rapidly depleted from the mesotrophic and oligotrophic waters with a halving time < 1 h. Only a small proportion of the DOS removed from solution was mineralized and excreted as SO_4^{2-} ($< 16\%$ of the total taken up) suggesting that the DOS could be satisfying a demand for carbon (C) and S. In conclusion, even though inorganic S was abundant in freshwater, it appears that the aquatic communities retained the capacity to take up and assimilate DOS.

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Introduction

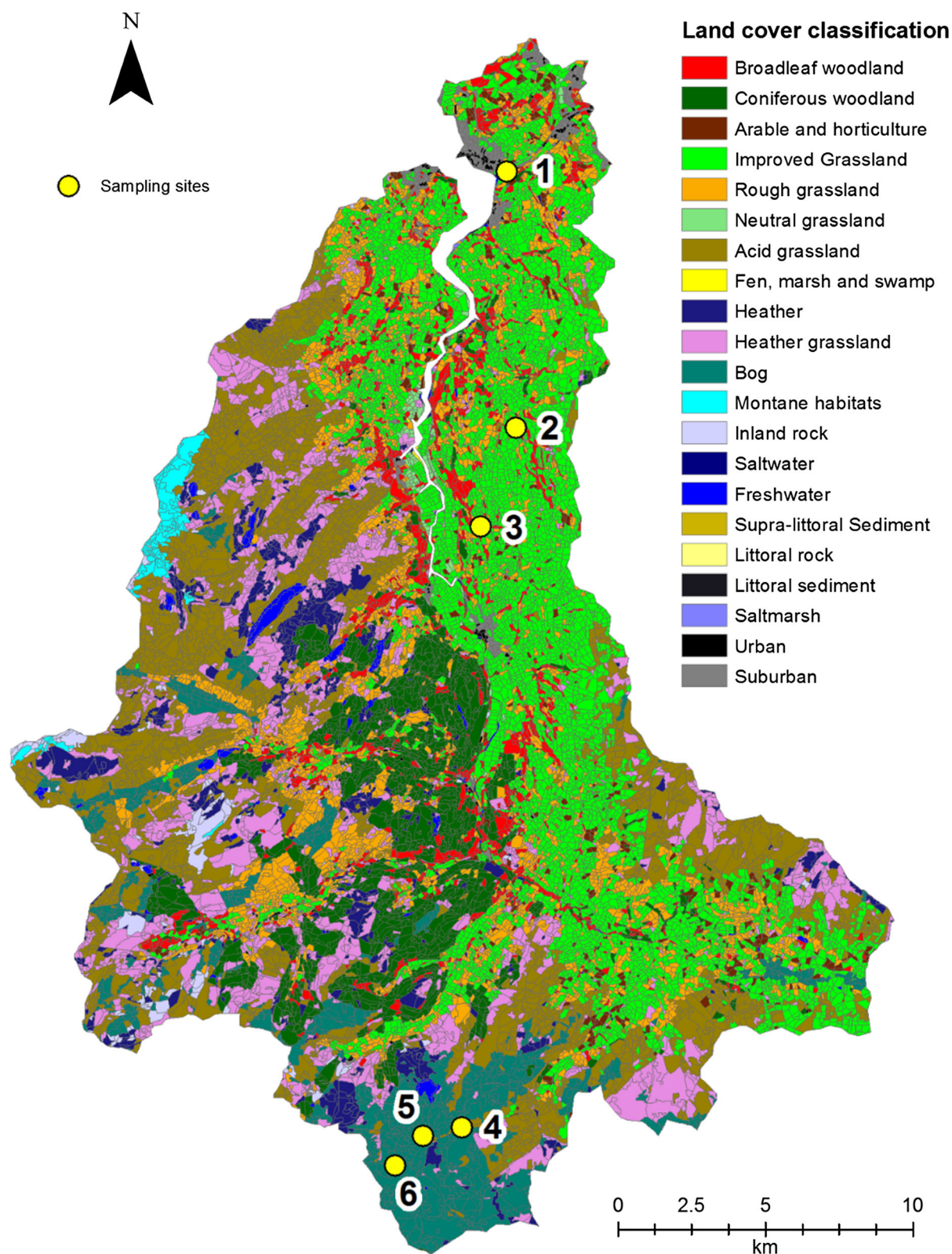
Carbon (C), nitrogen (N) and phosphorus (P) have long been considered to be the key macronutrients regulating primary productivity in freshwater environments. Although S is rarely limiting in freshwaters (Dodds and Whiles 2010), recent stoichiometric studies have found that average cellular sulphur (S) requirements are close to that of P (C:N:P:S 124:16:1:1.3; Ho et al. 2003; Ksionzek et al. 2016). As the C, N, P and S cycles are intrinsically linked through dissolved organic matter (DOM), it is therefore important to consider the cycling of dissolved organic sulphur (DOS). Further, through S-containing peptides, DOS may also play a role in the transport and bioavailability of trace metals (Marie et al. 2015; Ksionzek et al. 2016). Despite the lack of studies on DOS, the concentration of dissolved and particulate forms of organic S has been shown to exceed that present in an inorganic form (i.e. SO_4^{2-}) in some ecosystems (Levine 2016; Ksionzek et al. 2016). Whilst research has been undertaken to characterise DOS in the marine environment, comprehensive studies of the composition of aquatic DOS pools are lacking (Ksionzek et al. 2016). However, some compounds have been frequently identified and are considered to be of importance in overall S cycling (e.g. S-containing amino acids, dimethylsulfoniopropionate, DMSP) (Ginzburg et al. 1998; Sela-Adler et al. 2016).

Of the S-containing amino acids, only methionine and cysteine are biosynthetically incorporated into proteins and these are expected to represent the main forms of DOS entering unpolluted freshwaters (Brosnan and Brosnan 2006). Relative to other amino acids, they are generally present at low concentrations in the cell (ca. 1.5–3.5% of the total amino acid pool; Okayasu et al. 1997). However, they are also precursors for many other cellular metabolites, which can be present at high concentrations. For example, S-adenosyl methionine (SAM) is a co-factor involved in the majority of methyl transfer reactions across all organisms, *N*-formyl methionine acts as the translation

Fig. 1 Land cover map of the Conwy catchment with lowland improved grassland sites (1–3) and upland peat bog sites (4–6) indicated. Created with ArcGIS Hydrology toolbox (ESRI 2018, Version 10 Redlands, CA) using LCM2007 data provided by the Centre for Ecology and Hydrology (Emmett et al. 2016). Reproduced Brailsford et al. (2019)

initiator in prokaryotic protein synthesis and S-methylmethionine is a precursor for DMSP (Brosnan and Brosnan 2006; Ferla and Patrick 2014; Sela-Adler et al. 2016). The main role of cysteine is the creation of complex protein structures through the formation of disulphide bonds with other cysteine residues while methionine plays a key role in the initiation of protein translation and often forms part of the hydrophobic core of proteins (Brosnan and Brosnan 2006; Ferla and Patrick 2014). Cysteine may also be used to synthesize methionine in prokaryotes, a process that is reversed in eukaryotic cells (Cooper 1983; Ferla and Patrick 2014; Qiao et al. 2018).

Total DOS and particulate organic S (POS) concentrations in freshwater are rarely reported due to challenges in their measurement, however, measurements of total thiol concentrations (R-SH group; 10–160 nM) indicate their potential importance in long-distance S transport (Marie et al. 2015). In contrast, measurements of individual free S-containing amino acids in the water column indicate that they are only present at extremely low concentrations (0.2–5.0 nM; Horňák et al. 2016), despite their presence in cells at much higher concentrations (Li et al. 2017). This suggests that they may be rapidly cycled within freshwaters. We have not identified any previous work investigating the depletion of DOS compounds from aquatic environments or how this compares to inorganic sulphate depletion. The aims of this study were therefore to use ^{35}S -labelled isotopic tracers to: (1) quantify rates of DOS depletion in aquatic ecosystems; (2) compare the rates of depletion of DOS compounds (S-containing amino acids) versus inorganic S (SO_4^{2-}) in river waters, and (3) identify differences in S depletion in two contrasting land cover types.



Materials and methods

Field site

Samples were collected in the spring of 2018, from three independent streams draining each of two contrasting land cover types within the Conwy catchment, Wales, UK (Fig. 1; Emmett et al. 2016). Three replicate 1 L mid-stream samples were collected manually from 5 cm below the surface at each site in high-density polyethylene (HDPE) bottles. Samples were kept on ice in the dark during transportation to the laboratory and experiments commenced within 6 h. The first set of samples were collected from mesotrophic streams passing through lowland agricultural grasslands, subject to moderate livestock grazing and fertiliser applications. The second set were collected from three independent oligotrophic headwater streams draining an upland blanket peat bog dominated by acid heathland vegetation, with low intensity sheep grazing and no history of fertiliser application. General water and sediment characteristics of these sites have been previously described (Table 1; Brailsford et al. 2019; Yates et al. 2019).

Chemical characteristics

Thiol concentrations in river water samples were measured using a thiols fluorescent detection kit with an N-acetylcysteine standard (Lot: 18S037A; Invitrogen Inc., Carlsbad, CA). Total reflection X-ray fluorescence (TXRF) elemental analysis of underlying river sediments was measured on dried (40 °C), sieved (< 125 µm) sediment using a Bruker S2 Picofox TXRF spectrometer (Bruker Inc., MA, USA). The quantification of sulphate was conducted on river water samples by ion chromatography using a 930 Compact IC Flex (Metrohm, Herisau, Switzerland).

³⁵S-labelled nutrient depletion assays

Within 6 h of collection, aliquots of unfiltered river water (25 mL) were placed in sterile 50 mL polypropylene centrifuge tubes (Corning Inc., Corning, NY). Each sample was spiked with 200 µL of e-pure water (18 MΩ resistance) containing ³⁵S labelled methionine, cysteine or sodium sulphate (Na₂³⁵SO₄) to give a final activity 0.2 kBq mL⁻¹. Compounds were chosen to reflect possible organic (methionine, cysteine) or inorganic (Na₂³⁵SO₄) S compounds typically released during the breakdown of particulate organic matter entering soils and

Table 1 Chemical characteristics of the water samples used in the study

	Lowland mesotrophic	Upland oligotrophic	F	P value
Sulphate (mg S L ⁻¹)	0.11 ± 0.01	0.11 ± 0.02	0	0.877
Total free thiols (ng S L ⁻¹)	12.7 ± 3.9	BLD	–	–
pH	7.09 ± 0.08	4.20 ± 0.16	14	< 0.001*
Electrical conductivity (µS cm ⁻¹)	191 ± 8	49 ± 5	13	< 0.001*
Temperature (°C)	7.53 ± 0.37	9.00 ± 0.65	3	0.421
Dissolved organic C (mg C L ⁻¹)	2.86 ± 0.13	7.60 ± 0.62	6	< 0.001*
Total free carbohydrates (mg C L ⁻¹)	0.11 ± 0.02	0.09 ± 0.02	1	0.450
Total phenols (mg C L ⁻¹)	2.27 ± 0.66	1.78 ± 0.74	0	0.667
Total dissolved N (mg N L ⁻¹)	2.13 ± 0.24	0.38 ± 0.02	7	< 0.001*
NH ₄ ⁺ (mg N L ⁻¹)	0.05 ± 0.01	0.06 ± 0.01	0	0.818
NO ₃ ⁻ (mg N L ⁻¹)	1.73 ± 0.24	0.02 ± 0.00	7	< 0.001*
Total free amino acids (mg N L ⁻¹)	0.10 ± 0.01	0.13 ± 0.01	2	0.142
Molybdate-reactive P (mg P L ⁻¹)	0.07 ± 0.01	0.03 ± 0.00	4	< 0.001*

Values represent means ± SEM, rows 1–3 are *n* = 3, rows 4–11 are *n* = 9. *Denotes a significant *P* value when comparing the two sites. The significance level was set at *P* < .05. Rows 4–11 reproduced Brailsford et al. (2019). BLD indicates below the limit of detection (< 1 ng S L⁻¹)

freshwaters. We assumed that the amount of ^{35}S -isotope added to the water ($< 0.1 \text{ nM}$) did not change the intrinsic concentration of the pool being measured. Sterile controls run with e-pure water in place of river water resulted in no loss of ^{35}S -compounds from solution (Supplementary Fig. S1).

After sealing with sterile caps, the samples were subsequently incubated on a shaker (200 rev min^{-1}) in the dark at 10°C for the duration of the experiment. This temperature represents the mean annual temperature within the Conwy catchment (Brailsford et al. 2019). A headspace of at least 25 mL was maintained throughout the experiment in order to prevent samples from becoming anoxic. After incubation for 1, 2, 4, 6, 24, 48, 72, 144 h, two 1.0 mL aliquots were removed from the tubes and centrifuged to remove microbial cells ($20,817\times g$, 3 min). 0.5 mL of the supernatant was either: (1) placed directly into a scintillation vial for ^{35}S quantification, or (2) added to 0.5 mL BaCl_2 (0.5 M) and centrifuged again ($20,817\times g$, 3 min) to precipitate and remove any inorganic sulphate present in the methionine and cysteine treatments (i.e. S mineralized from DOS and present in the external media) and the supernatant of the BaCl_2 treatment placed into a scintillation vial. The subsamples were then mixed with Optiphase HiSafe 3 scintillation cocktail (4 mL; PerkinElmer Inc., Waltham, MA) and the ^{35}S quantified on a Wallac 1404 liquid scintillation counter with automated quench correction (Wallac EG&G, Milton Keynes, UK).

Data analysis

Data analysis was carried out in SPSS v22 (IBM UK Ltd., Portsmouth, UK). DOS values were corrected for any cleaved sulphate groups remaining in solution and analysis of covariance (ANCOVA) was used, with sample time as continuous variable, the ^{35}S tracer added as a categorical variable and the percentage of ^{35}S tracer remaining in solution as the dependent variable. One-way ANOVA was used to detect differences between depletion kinetic parameters derived from the curve-fitting, with a significance level set at $P < .05$. Graphs and curve-fitting data were produced using Sigmaplot v13.0 (Systat Software Inc., San Jose, CA). To determine the halving time ($t_{1/2}$) and decay coefficient (k) of each S compound in river water, single first order exponential decay curves with an asymptote were fitted to the data according to:

$$s = y_0 + (a \times \exp^{-kt}), \quad (1)$$

where s is the ^{35}S remaining in solution, y_0 represents an asymptote (%), k is the exponential decay coefficient describing ^{35}S removal from solution, a is the reactive sulphur pool size (%) and t is time (h) (Hill et al. 2008). The halving time ($t_{1/2}$) of each S form can then be calculated as:

$$t_{1/2} = \ln(2)/k. \quad (2)$$

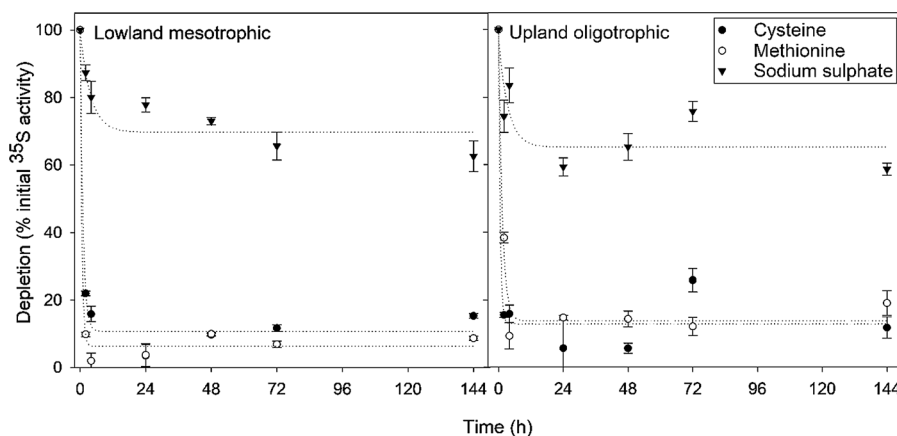


Fig. 2 Depletion of either ^{35}S -labeled DOS compounds (cysteine, methionine) or inorganic sulphur ($\text{Na}_2^{35}\text{SO}_4$) after addition to lowland mesotrophic and upland oligotrophic river water. Values represent means \pm SEM ($n = 3$)

Table 2 Model parameters describing the size and turnover of ^{35}S over time for lowland mesotrophic and upland oligotrophic systems

	Lowland mesotrophic			Upland oligotrophic			<i>P</i> value
	Cysteine	Methionine	Sodium sulphate	Cysteine	Methionine	Sodium sulphate	
y_0	$13.7 \pm 1.8^{\text{a,b}}$	$8.9 \pm 0.8^{\text{a}}$	$70.0 \pm 1.5^{\text{d}}$	$16.6 \pm 0.5^{\text{b,c}}$	$20.4 \pm 1.6^{\text{c}}$	$65.2 \pm 1.1^{\text{d}}$	$< 0.001^*$
a	$86.3 \pm 1.9^{\text{c,d}}$	$91.1 \pm 0.8^{\text{d}}$	$28.8 \pm 1.8^{\text{a}}$	$83.4 \pm 0.5^{\text{b}}$	$78.9 \pm 1.3^{\text{b}}$	$30.2 \pm 0.8^{\text{a}}$	$< 0.001^*$
k	$1.11 \pm 0.18^{\text{a,b,c}}$	$2.36 \pm 0.05^{\text{c}}$	$0.20 \pm 0.03^{\text{a}}$	$2.06 \pm 0.78^{\text{b,c}}$	$0.89 \pm 0.27^{\text{a,b}}$	$0.17 \pm 0.06^{\text{a}}$	$< 0.001^*$
$t_{1/2}$ (h)	$0.64 \pm 0.11^{\text{a}}$	$0.29 \pm 0.01^{\text{a}}$	$3.67 \pm 0.65^{\text{a,b}}$	$0.39 \pm 0.15^{\text{a}}$	$0.93 \pm 0.27^{\text{a}}$	$4.80 \pm 1.32^{\text{b}}$	0.003^*
r^2	0.95 ± 0.01	0.99 ± 0.00	0.74 ± 0.05	0.89 ± 0.03	0.86 ± 0.04	0.63 ± 0.03	–

The models are described by a single first order exponential decay equation fitted with an asymptote. Values represents means SEM ($n = 3$)

Results and discussion

Sulphur composition in two contrasting land-cover types

In the current study, thiol concentrations were much lower than reported in previous studies, being 0.4 nM for mesotrophic rivers and below the limit of detection (< 0.05 nM) for the upland oligotrophic rivers. The former is two orders of magnitude lower than values presented in other studies of freshwaters detected using a static mercury drop electrode (Superville et al. 2013; Marie et al. 2015; Table 1). Sulphate concentrations were similar across the mesotrophic and oligotrophic rivers (3425 ± 265 versus 3415 ± 583 nM; one-way ANOVA, $F_{1,4} = 0.161$, $P = 0.709$). Although we did not identify individual amino acids, the total concentration of free amino acids was similar between the two river types (7.38 ± 0.24 versus 9.04 ± 0.95 μM).

^{35}S -labelled depletion

In the current study, the addition of trace amounts of S-containing amino acids resulted in a rapid depletion from the dissolved fraction for both mesotrophic and oligotrophic waters, whereas $\text{Na}_2^{35}\text{SO}_4$ was not readily depleted from solution in either treatment (Fig. 2). However, the higher background inorganic S concentrations present in both mesotrophic and oligotrophic waters will have diluted the isotope pool, reducing the depletion of $\text{Na}_2^{35}\text{SO}_4$ from solution. For both mesotrophic and oligotrophic waters, the compound added had a significant interaction with time, resulting

in a difference in depletion over time between S-containing amino acids (cysteine, methionine) and sodium sulphate (ANCOVA, $F_{1,7} = 17$, $P < .0001$ and $F_{1,7} = 16$, $P < .0001$ respectively). Overall, very little of the ^{35}S -label present in the amino acid was released into solution as $^{35}\text{SO}_4^{2-}$ ($15.2 \pm 3.7\%$ of the total added), indicating that the majority of the S remaining in solution had not been completely cleaved from the carbon skeleton. Similarly, a study of S availability to plants in paddy field soils demonstrated higher rates of depletion from ^{35}S incorporated into the organic components of rice straw compared to S addition as $\text{Na}_2^{35}\text{SO}_4$ (Zhou et al. 2006).

In the lowland mesotrophic waters, the rate of methionine depletion from solution appeared higher than that of cysteine, with a reversal of this trend observed in the upland oligotrophic waters. Overall, however, there were no statistically significant differences between the rates of cysteine and methionine depletion from solution, according to the calculated k coefficients (Table 2). The rate of cysteine removal from solution (k) was ca. twice as fast in the upland oligotrophic waters compared to lowland mesotrophic waters, while the reverse was true for methionine (Table 2). The k coefficients determined here for DOS compounds were the same order of magnitude as those previously observed for DON and DOP compounds in rivers and DOC in soil systems (Hill et al. 2008; Islam et al. 2013; Glanville et al. 2016). Similar trends were observed for calculated $t_{1/2}$ values; the $t_{1/2}$ for methionine was quicker than for cysteine, whereas the reverse was true for upland oligotrophic waters, although not statistically significant (Table 2). This was reflected in

an increase in $t_{1/2}$ for methionine and a decrease in $t_{1/2}$ for cysteine from lowland to upland waters. In all treatments, the $t_{1/2}$ for the DOS compounds was < 1 h. A rapid initial loss of inorganic S ($\text{Na}_2^{35}\text{SO}_4$) from solution was observed, with more depletion observed in upland oligotrophic rivers compared to lowland mesotrophic rivers (Table 2). However, depletion did not fall below 50% in mesotrophic or oligotrophic waters, therefore the calculated $t_{1/2}$ values should be treated cautiously (Fig. 2; Table 2). We attribute this lack of SO_4^{2-} depletion to the limitation of the aquatic microbiota by another nutrient, such as carbon, or a lack of available electron acceptors.

It has generally been considered that inorganic S forms, in addition to cysteine, are the preferred source of S for the microbial biomass, although fungal species may also use methionine as a preferred source (Kertesz 2000). Previous community analysis of the rivers in the current study found that $< 5\%$ of phospholipid-derived fatty acids (PLFAs) originated from a fungal source, suggesting that the rapid cysteine depletion cannot be ascribed to high proportions of fungal cells within the microbial community (Brailsford et al. 2019). There is literature to support the presence of sulphate starvation induced (SSI) proteins, which are synthesised by a range of cultures of microorganisms when preferred sources of S are not available (Stipanuk 1986; Kertesz et al. 1993; Scott et al. 2007). These enzymes allow other sources of S to be used, altering S cycling in sulphate-limited conditions, however, the SO_4^{2-} trigger concentration at which their expression occurs in aquatic environments remains unknown.

The current study measured the biotic removal of methionine, cysteine and $\text{Na}_2^{35}\text{SO}_4$ from freshwaters in isolation at low concentrations. Further studies spanning a broader range of aquatic physicochemical gradients could help to identify the key drivers of changes in DOS depletion from solution (e.g. nutrient concentrations, pH). The mesocosm experiment in this study was undertaken in the dark in order to determine the response of heterotrophic organisms to S addition, however autotrophic microorganisms could respond differently to aquatic S inputs. A low percentage of ^{35}S -labelled DOS added was re-released as cleaved $^{35}\text{SO}_4^{2-}$, suggesting in the current study DOS was not being taken up by the aquatic microbiota to meet C/N requirements alone. In future studies, we suggest using

^{14}C - and ^{15}N -labelled DOS alongside ^{35}S compounds to provide further insights into the fate of the C skeleton of DOS compounds. In addition, using a broader range of tracer concentrations would allow the determination of the maximal depletion capacities and nutrient spiralling rates of DOS compounds in aquatic ecosystems, in order to advance our understanding of the capacity for depletion of S-containing amino acids by aquatic microbiota. A previous study of amino acid metabolism of *Streptococcus thermophilus* in batch fermentations, combining metabolomic and transcriptomic approaches, observed increases in enzymes associated with both cysteine and methionine depletion, despite both amino acids being added to the nutrient broth. This suggests that the rate of depletion from solution may not meet microbial demand for S-containing amino acids (Lahtvee et al. 2011; Qiao et al. 2018). The combination of radiolabelled tracers in conjunction with omics approaches could provide additional insights of the pathways involved in S depletion and metabolism.

Conclusions

In summary, the results of this study go against the consensus that sulphate is the preferred source of S for most microorganisms (Kertesz 2000). We found that the S-containing amino acids cysteine and methionine were rapidly removed from solution, whereas inorganic sulphur ($\text{Na}_2^{35}\text{SO}_4$) depletion was limited. Halving times for the compounds in solution were < 1 h in both mesotrophic and oligotrophic rivers. Limited abiotic depletion of ^{35}S tracers was observed, therefore we hypothesise that this removal from solution is due to uptake by the aquatic microbiota, as it is more energetically efficient to take up free amino acids and directly incorporate them in proteins in comparison to the uptake of SO_4^{2-} and de novo amino acid biosynthesis. This is especially the case for S-containing amino acids which are energetically costly to produce in comparison to other amino acids (Akashi and Gojobori 2002). As the DOS compounds studied here represent a tri-nutrient source (C, N and S) these low molecular weight forms of S also negate the need to take up as much inorganic N. Further work is required to a wider range of DOS compounds and also to quantify their rates of production. This will

enable a quantitative assessment of the overall role of DOS in freshwater S cycling.

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